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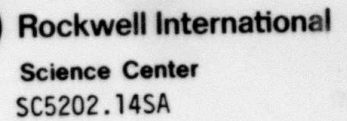
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SUMMARY

Thick  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  films ( $> 5 \mu\text{m}$ ) were deposited on  $\text{CdTe}$   $\langle 111 \rangle$  and  $\langle 111 \rangle$  other substrates by evaporating either  $(\text{HgTe})_{1-x}/(\text{CdTe})_x$  mixture or  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  crystals with a pulsed laser. The films were single phase and stoichiometric. All films showed preferential  $\langle 111 \rangle$  texture. Electrical properties were characterized by Hall measurements, for a  $x = 0.3$  film after annealing, typical values of carrier concentration and mobility were  $1-2 \times 10^{17}/\text{cm}^3$  and  $3500-6000 \text{ cm}^2/\text{Vsec}$ , respectively.

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## 1.0 INTRODUCTION

### 1.1 Program Objectives

The main objective of this program is to explore and develop a novel thin film technique (LADA). In this technique, a pulsed laser is used as the power source for evaporation and in situ beam processing. It will be demonstrated for two materials:  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and  $\text{ZnO}$ .

### 1.2 Overall Plan

The program started in February 1979. The work performed during the first two years involved exclusively with  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ . Accomplishments included the design, construction and debugging of a new apparatus and carrying out experiments to study the evaporation-deposition mechanism of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ .

Second phase started in May 1980.  $\text{ZnO}$  was added as a new material to the program. A separate system will be built for  $\text{ZnO}$  in order to prevent intercontamination between the two materials. The new apparatus has not yet been completed. Therefore, this manuscript reports mainly the progress on the  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  work.



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1.3 Accomplishments

Accomplishments in this period are:

1. A new LADA system for depositing ZnO has been designed and is being fabricated by the Torr Vacuum, Inc. A CO<sub>2</sub> laser will be used as a power source. This laser (Model 540, Apollo Laser, Inc.) has a maximum cw output of 80 W at 10.6  $\mu\text{m}$ . It can also be operated in a pulsed mode with variable repetition rate and pulse width. This laser was chosen, because ZnO absorbs strongly at its radiation wavelength of 10.6  $\mu\text{m}$ . The system is expected to be operational in early January 1982.
2. The LADA system for Hg<sub>1-x</sub>Cd<sub>x</sub>Te has been modified. Major changes are a new target-substrate configuration, and new optical arrangement for coupling the laser energy into the target material. The purpose of these modifications is to increase the deposition rate and improve the systems reflexivity. Consequently, the deposition of thick (> 5  $\mu\text{m}$ ) Hg<sub>1-x</sub>Cd<sub>x</sub>Te film is now a routine process.
3. Two types of target sources ((HgTe)<sub>1-x</sub>/(CdTe)<sub>x</sub>, x = 0.3 and 0.35, and Hg<sub>1-x</sub>Cd<sub>x</sub>Te, x = 0.3) were used. Stoichiometric films were deposited on various substrates (CdTe, Si and sapphire) at different temperatures.



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4. Optical, structural and electrical properties of the films were characterized.



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## 2.0 TECHNICAL INFORMATION

### 2.1 Background

In the Final Report of Phase 1, the evaporation mechanism of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and its related compounds induced by pulsed laser irradiation was discussed. Under the proper laser condition (i.e., power density of mid  $10^6$   $\text{W}/\text{cm}^2$ , and fast scan rate).  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  can evaporate congruently. Most of the evaporants are atomic Hg, Cd and Te with the presence of a minute fraction ( $< 2\%$ ) molecular tellurium ( $\text{Te}_2$ ). Stoichiometric films could be deposited. However, the deposition rate was too low and not steady.

With the new modifications, a constant deposition rate can be maintained. Thick film can be prepared routinely.

### 2.2 Experimental Results

Two kinds of target materials were used: pressed pellets of  $(\text{HgTe})_{1-x}/(\text{CdTe})_x$  powder mixtures (Gallard Schlesinger Chemical Co.) and bulk  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  crystals (New England Research Center). X-ray diffraction analysis detected the presence of a second phase consisting of free tellurium in both materials. The free tellurium level in the  $(\text{HgTe})_{1-x}/(\text{CdTe})_x$  mixture was 2-3%, in bulk  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  crystals it was about 1%. However, in some portion of the bulk crystal, it was not detectable.

A deposition rate between 1-1.5  $\mu\text{m}/\text{hr}$  was used. The factors which limit the deposition rate will be discussed in Section 2.2.1.1.



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The experimental results will be presented in two parts. First, the conditions for depositing stoichiometric films will be discussed in Section 2.2.1. This will be followed by the discussion on the results of film characterization in Section 2.2.2.

### 2.2.1 Stoichiometric Control of the As-Deposited Film

#### 2.2.1.1 Effect of Hg Backpressure

In the previous report, we indicated that the presence of a Hg backpressure ( $P_{\text{Hg}}$ ) during the evaporation-deposition process was essential for the formation of a stoichiometric film. Since then, a more systematic study has been carried out.

In a series of experiments, we studied the film composition as a function of  $P_{\text{Hg}}$ . A piece of  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  crystal was used as target material. The deposition rate was  $1.2 \mu\text{m/hr}$  and the substrate was  $\text{CdTe} \langle 111 \rangle$  at room temperature.  $P_{\text{Hg}}$ , ranging from  $10^{-6}$  to  $2 \times 10^{-4}$  torr, was controlled by throttling a valve connecting a pool of mercury to the main chamber. The pressure readings were taken directly from an ionization gauge without any correction for the ionization efficiency of mercury.

Figure 1 shows an infrared transmission spectrum of a film deposited in the absence of Hg backpressure ( $< 10^{-6}$  torr). Instead of showing an absorption edge at  $4 \mu\text{m}$  as expected for a film with a stoichiometric  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  composition, the transmission cuts on at  $1.05 \mu\text{m}$ . This



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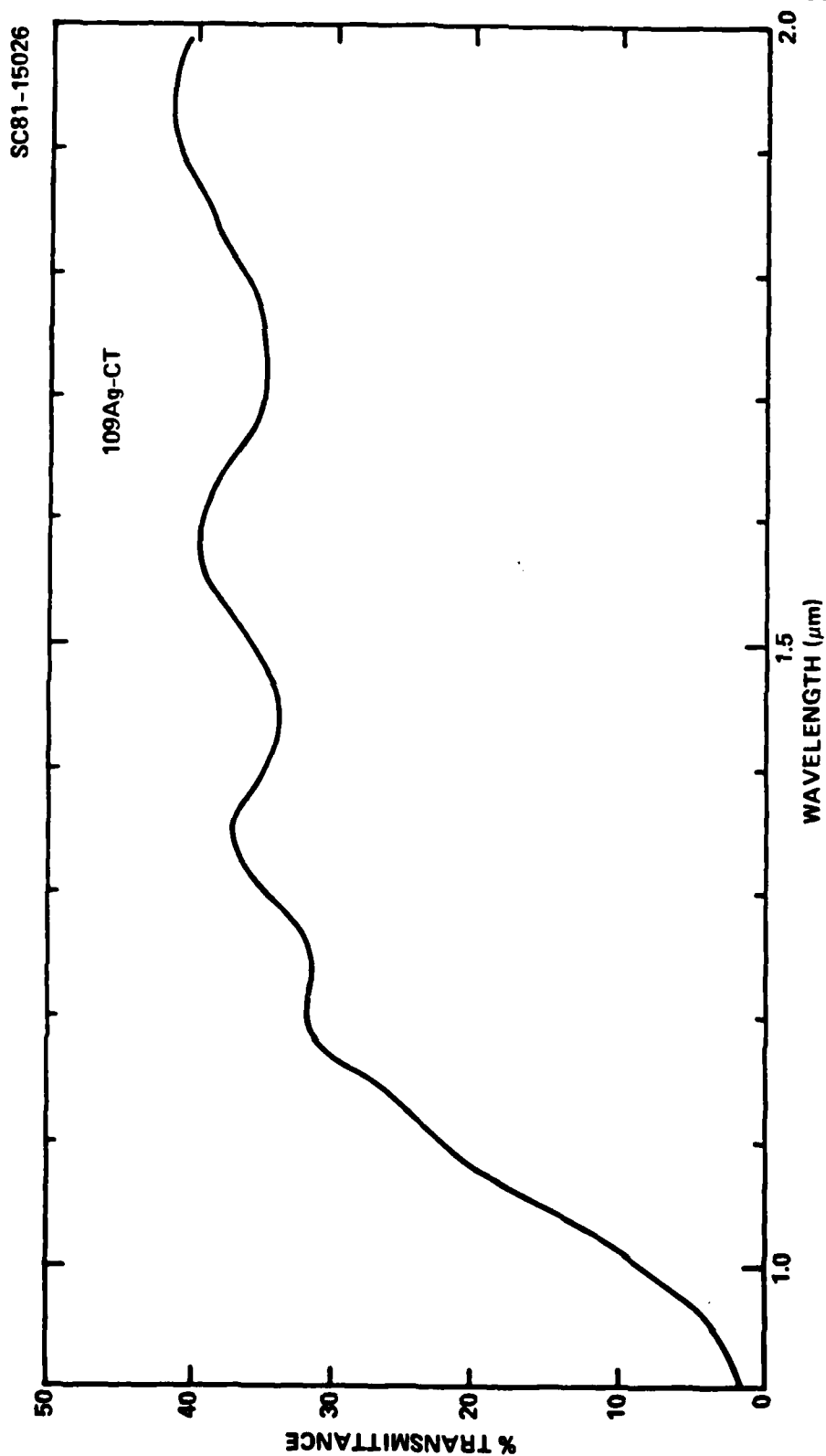


Fig. 1 Infrared transmission spectrum of a film deposited from a  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  target material in a Hg free vacuum.



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corresponds to a film with very low Hg content. EDAX measurements indicate its composition to be  $\text{Hg}_{0.06}\text{Cd}_{0.3}\text{Te}$ . By assuming the sticking coefficients of Cd and Te on a room temperature substrate to be unity, the sticking coefficient of Hg atoms will then be less than 0.1!

Hg discrepancy can be compensated by carrying out the deposition in a Hg backpressure. Hg contents  $f$ , expressed in terms of the fraction of stoichiometric Hg as in  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ , is plotted as a function of  $P_{\text{Hg}}$  in Fig. 2. The relationship is linear up to the saturation point. Under the condition of this experiment, the saturation point is a Hg pressure of  $8 \times 10^{-5}$  torr, above which stoichiometric  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  films can be formed. Within the pressure range studied here, the main free path is too long for the gaseous interaction to be important. Therefore, any effect on incorporating Hg atoms into the film must be due to a gas-surface interaction. A deposition mechanism can be postulated in the following.

After the target material of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  crystal or  $(\text{HgTe})_{1-x}/(\text{CdTe})_x$  mixture was irradiated with high power laser pulses, it evaporates congruently into atoms (Hg, Cd and Te) and a small amount of molecules ( $\text{Te}_2$ ). When these species impinge on to the substrate surface, Cd and Te ( $\text{Te}_2$ ) stick to the surface with a unit probability and react subsequently to form CdTe. The excess tellurium then reacts with Hg. Because of the weak HgTe bond, the probability for Hg to stay on the surface by HgTe formation is very low. The unreacted tellurium can be compensated by the background Hg. The amount of Hg back-pressure required to react with all the free tellurium depends on the flux of



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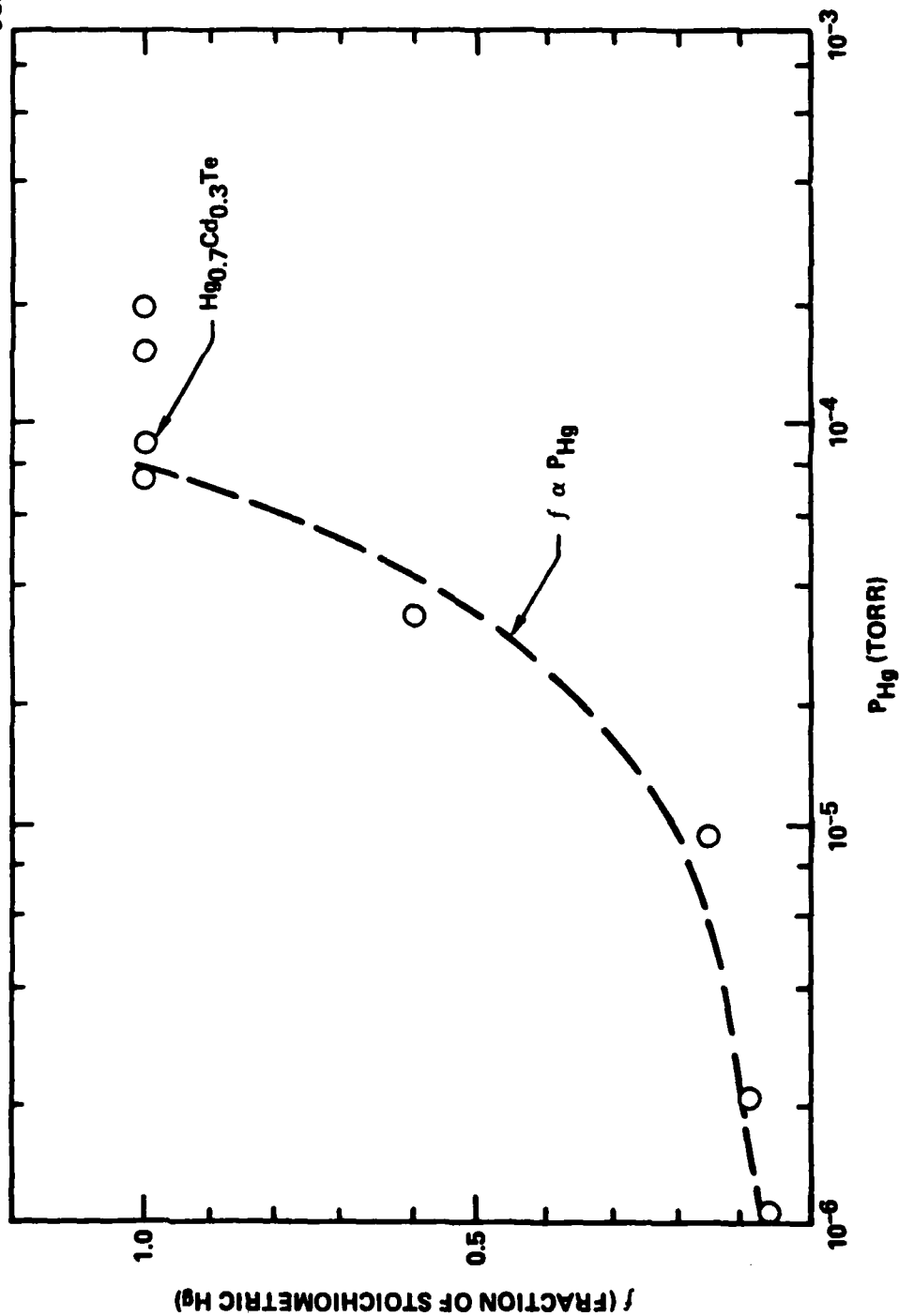


Fig. 2 Relationship between the mercury content in the film and mercury backpressure during the deposition.



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the evaporants and the substrate temperature. The amount of  $P_{Hg}$  which can be introduced into the vacuum system sets the upper limit of the deposition rate.

#### 2.2.1.2 Beam Composition Profile

Thin film deposition by pulsed laser induced evaporation is a new technique. There are still some unanswered fundamental questions. Two the the most basic questions are: What is the angular distribution of the evaporants? Is the composition uniform in all directions? The second question is particularly important, because it relates directly to the composition uniformity of the film.

A simple experiment was carried out to elucidate these questions. A piece of  $Hg_{0.7}Cd_{0.3}Te$  bulk crystal was evaporated by laser pulses onto a number of CdTe substrates placed at different angles. The Hg backpressure in the system during deposition was at  $2 \times 10^{-4}$  torr, high enough to assure the formation of stoichiometric films. After deposition for five hours, the film thicknesses were measured and their composition were determined by the infrared transmission spectra.

The film thickness is directly proportioned to the beam intensity. It is plotted as a function of the angular location in a polar coordinate shown in Fig. 3. It was found to obey a  $\cos^6\theta$  relationship instead of the usual  $\cos \theta$  law countered in other types of evaporations. Similar angular dependence was also observed in a different experiment<sup>1</sup> where a pulsed  $CO_2$  laser was used to evaporate triglycine sulfate.

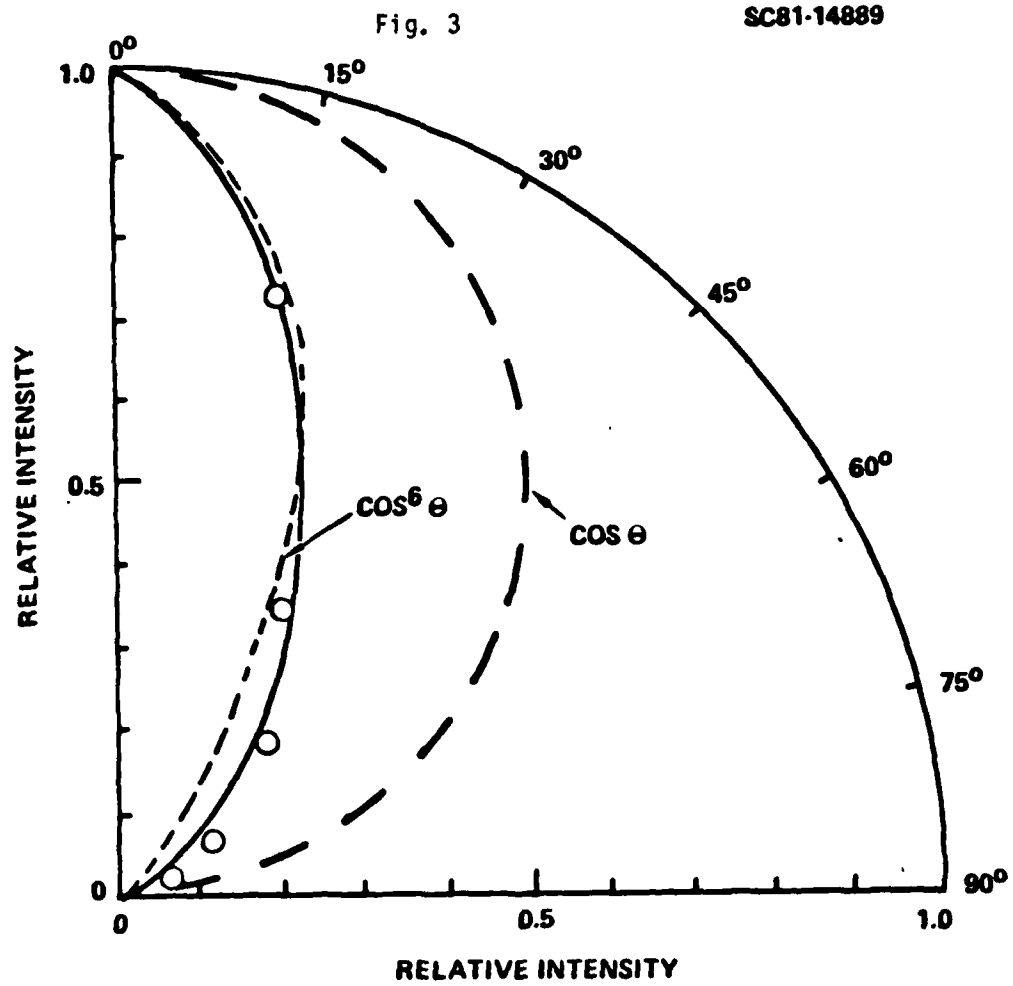


Fig. 3 Angular profile of a laser evaporated beam.



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The transmission spectra of the films deposited at various angles are shown in Fig. 4 for comparison. All the films have absorption edge at the same location, an indication of uniform composition in all directions. This has two implications.

1. The films should have good lateral compositional uniformity.
2. This technique has the potential for mass production. Many wafers can be led into the vacuum and deposited during a single run, thus increasing the yield and reduce the cost. On the contrary, other existing thin film deposition techniques only have a limited useful area for substrate mounting. In MBE,<sup>2</sup> this area is defined by the interception of three elemental beams. In sputtering,<sup>3</sup> the substrate area is limited by the plasma confinement.

#### 2.2.2 Thin Film Characterization

Thin films were characterized optically (IR transmission), structurally (x-ray diffraction) and electrically (Hall measurement). Different post annealing conditions were also studied.

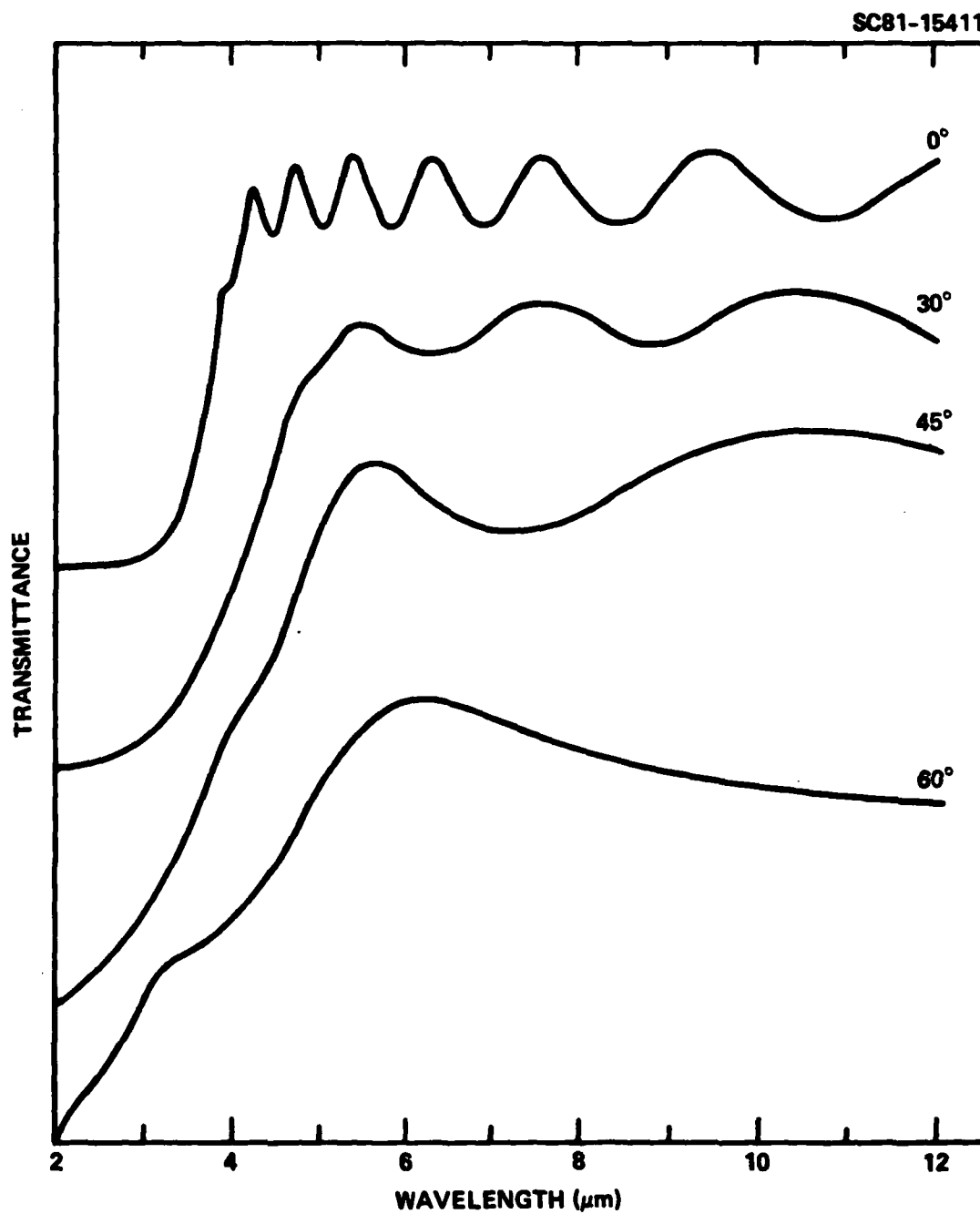


Fig. 4 IR transmission spectra of films deposited at various angles to the target.



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#### 2.2.2.1 Optical Properties

Films deposited from  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  bulk crystals showed different IR absorption characteristics from those deposited from the  $(\text{HgTe})_{1-x}/(\text{CdTe})_x$  powder mixtures.

2.2.2.1.1. Films from Bulk  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  Crystals. Bulk  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  crystal from New England Research Center were used. They were sliced, polished and finally etched in  $\text{Br}_2$ /methanol solution. The slices were 12 mm in diameter and 3 mm thick. Each slice can yield a film about 10-15  $\mu\text{m}$  thick on a substrate placed at 3 inches away. Before the deposition took place, the target material was cleaned by scanning the focused laser spot over the surface for about 10 min in order to remove the material from the top layer. Laser power densities were in the mid  $10^6 \text{ W/cm}^2$  range, repetition rate at 15 KHz and a Hg backpressure at  $1.5 \times 10^{-4}$  torr. Under this condition, the deposition rate was between 1.0  $\mu\text{m}$ -1.5  $\mu\text{m/hr}$ .

Figure 5 shows the IR transmission spectra at the corners and the center of a thin film 1-1/2 cm  $\times$  1-1/2 cm in size. Good lateral compositional uniformity is indicated by the agreements in the cut-on wavelengths. The peaks in the transmission part of the spectra are due to optical interference of the reflections from the substrate-film interface and the film surface. Film thickness can be calculated from the locations of these peaks by using a refractive index of  $n = 3.43$  for  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ . The values were compared to the Dektak measurements. The agreement was within 10%. Thickness non-uniformity of this film was found to be about 3%.



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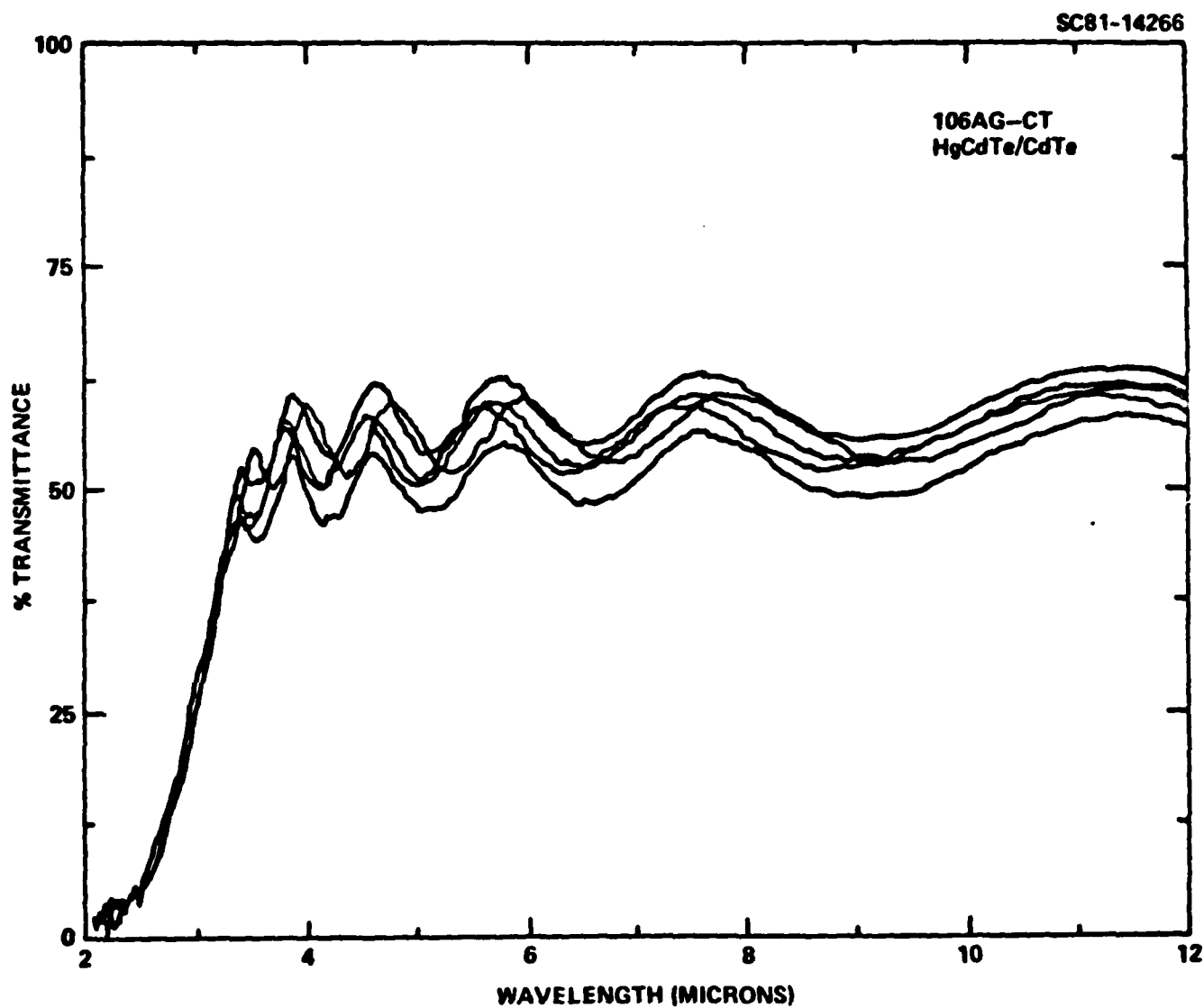


Fig. 5 IR transmission spectra at five locations of a HgCdTe film.



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2.2.2.1.2 Films from  $(\text{HgTe})_{1-x}/(\text{CdTe})_x$  Powder Mixtures. Pellets of powder mixture were prepared in the following way. Portions of HgTe and CdTe powders were weighed out according to the desired alloy composition. The mixture was then poured into a stainless steel capsule and mounted to a fixture. Mixing was accomplished by vibrating the fixture at 20 Hz with an amplitude of 1 cm for 15 min. The mixture was then cold pressed in an evacuated die at a pressure of 3 tons/cm<sup>2</sup> for 2 min. The finished pellets were 13 mm in diameter and 3 mm thick with a smooth, metallic finish. Two compositions,  $x = 0.3$  and  $x = 0.35$ , were tried. Deposited films were also annealed in a closed ampoule under Hg over pressure. Figure 6 shows two IR transmission spectra for a film deposited from the  $(\text{HgTe})_{0.75}/(\text{CdTe})_{0.25}$  mixture before and after annealing. Figure 7 shows spectra of films deposited from  $(\text{HgTe})_{0.7}/(\text{CdTe})_{0.3}$  mixture (after annealing) and  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  bulk crystal (as-grown) for comparison. The as-grown films deposited from powder mixtures have very gradual absorption edges. After thermal annealing, it becomes sharper but still not as sharp as those deposited from the bulk material.

2.2.2.1.3 Films on Foreign Substrates. Foreign substrates such as Si<111> and sapphire were also used. A piece of  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  bulk crystal was used as the target in these experiments. The IR transmission spectra are shown in Figs. 8 and 9. Sapphire becomes opaque at wavelengths longer than 7  $\mu\text{m}$ , therefore, when a  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  film was deposited, the overall transmission spectrum is similar to that of a narrow band filter.



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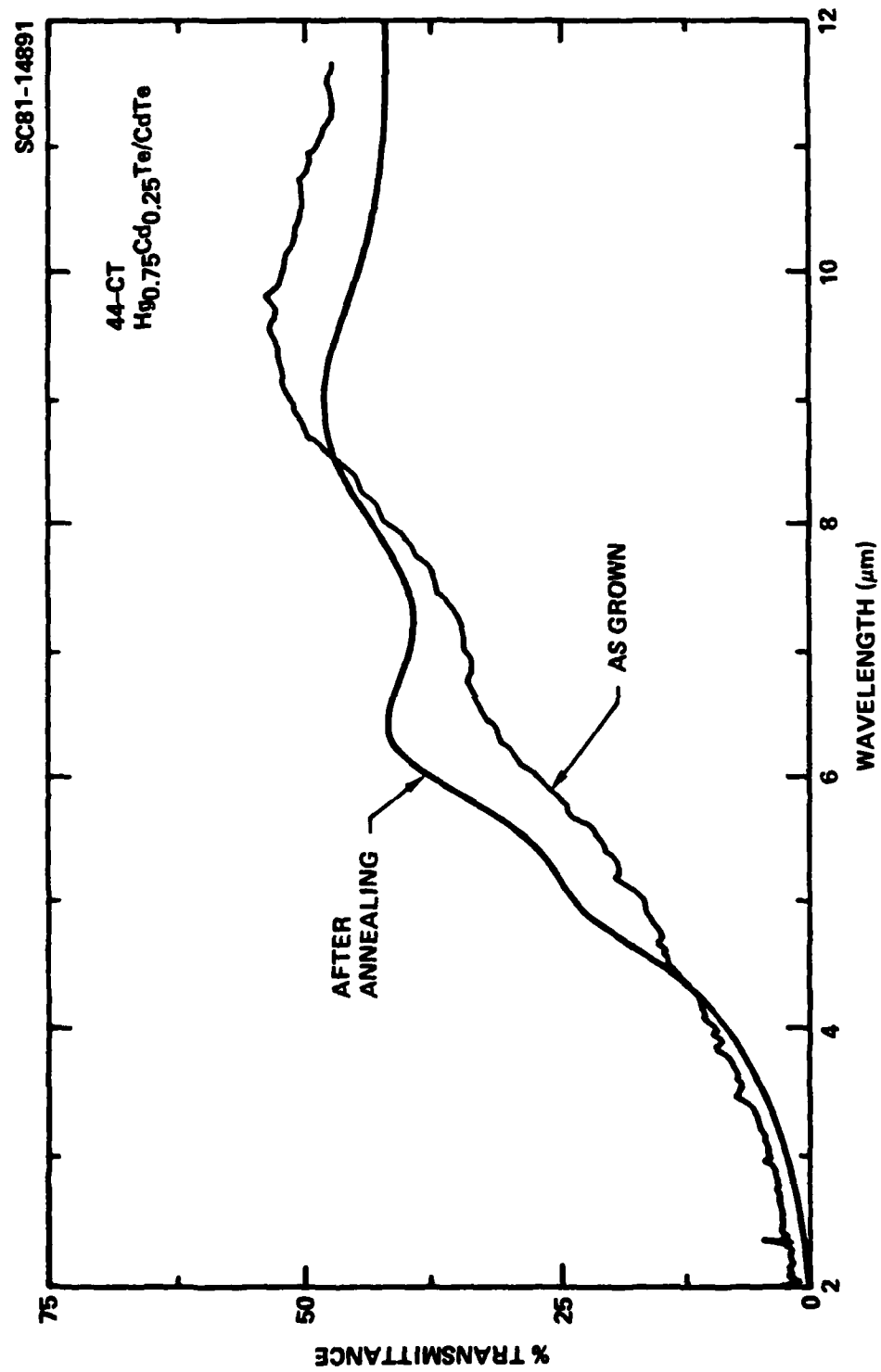


Fig. 6 Infrared transmission of a  $\text{HgCdTe}$  film on  $\text{CdTe}$  deposited from  $(\text{HgTe})_{0.75}/(\text{CdTe})_{0.25}$  mixture.



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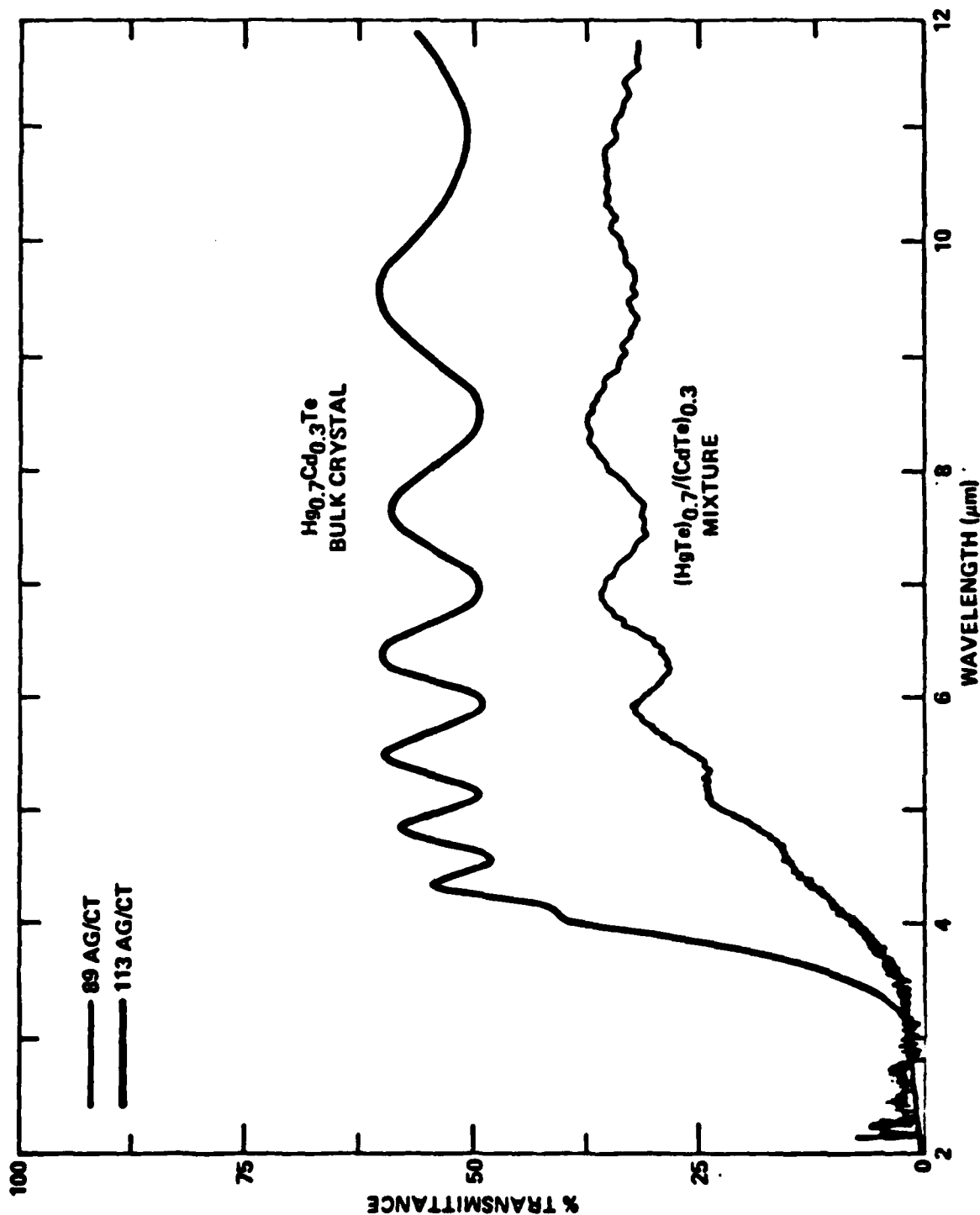


Fig. 7 IR transmission spectra of film deposited from Hg<sub>0.7</sub>Cd<sub>0.3</sub>Te crystal and (HgTe)<sub>0.7</sub>/(CdTe)<sub>0.3</sub> mixture.



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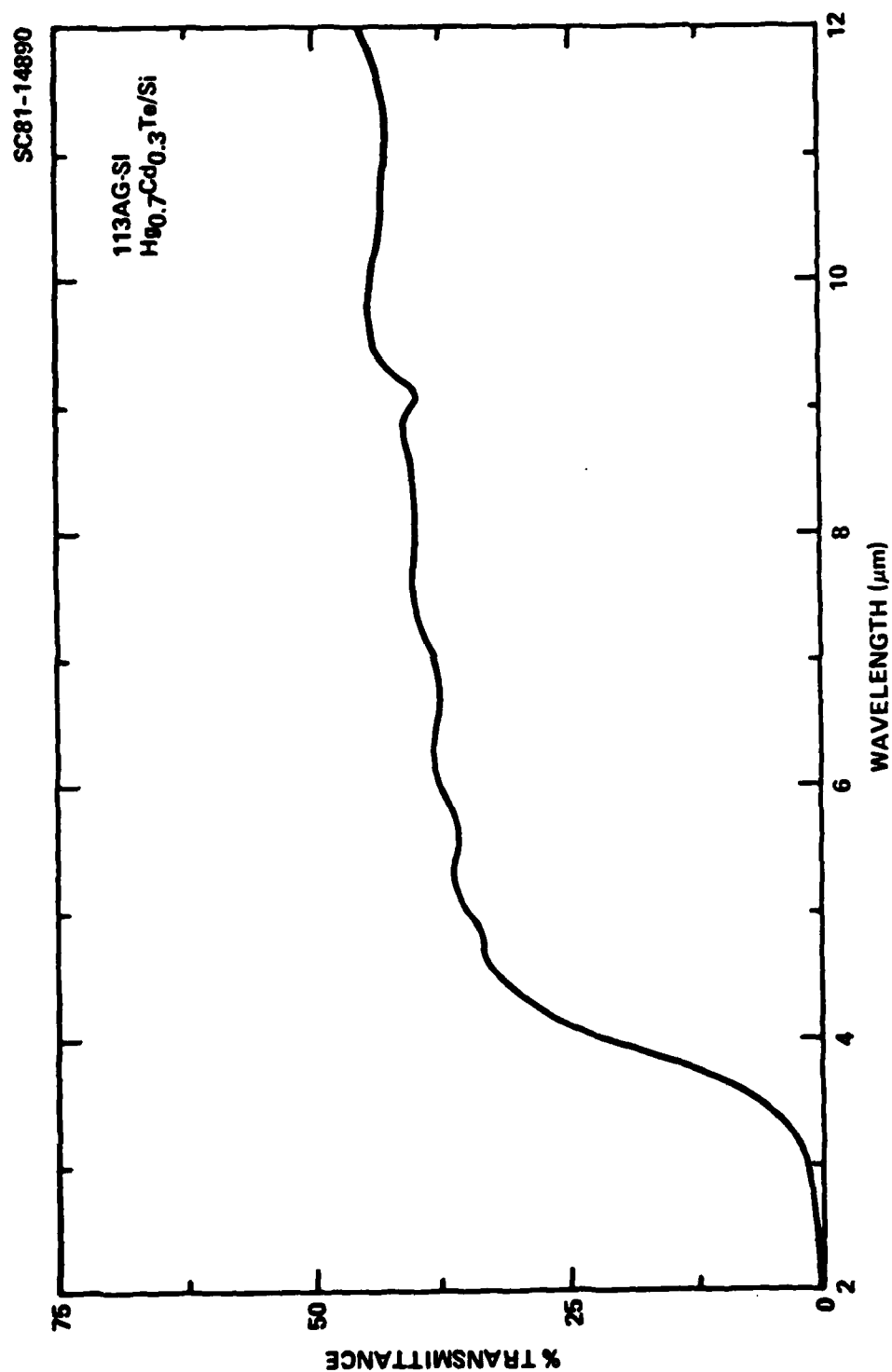


Fig. 8 IR transmission spectrum of a  $\text{HgCdTe}$  film deposited on Si.



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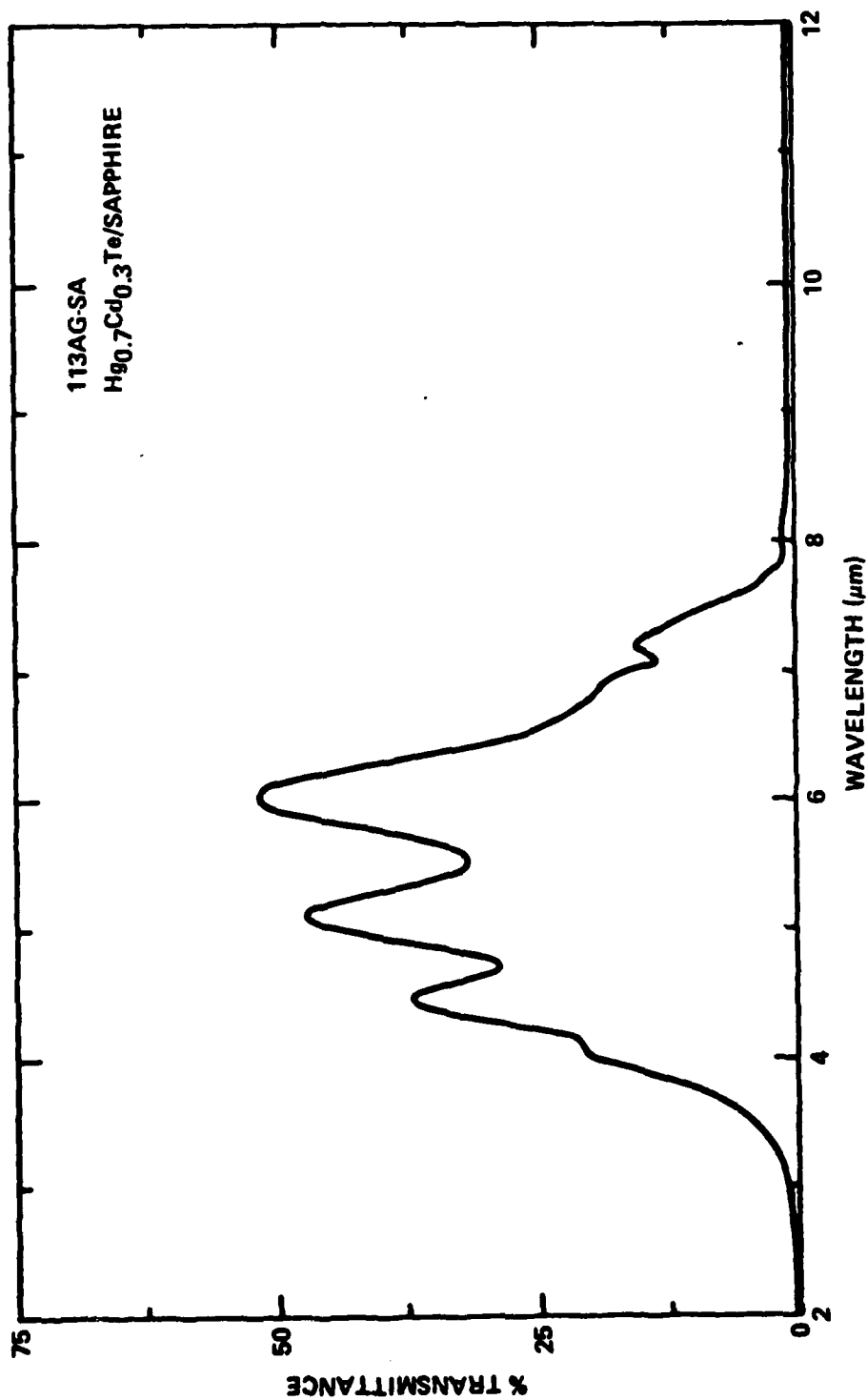


Fig. 9 IR transmission spectrum of a  $\text{HgCdTe}$  film deposited on sapphire.



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## 2.2.2.2 Structural Properties

2.2.2.2.1 Surface Morphology. Films deposited on various substrates at room temperature do not show any morphological difference. However, at higher temperature, it depends on the substrate material and orientation. Figure 10 shows two films deposited on CdTe  $\langle 111 \rangle$ A and Si  $\langle 111 \rangle$  substrates at 125°C. For films deposited on other substrates such as sapphire and mis-oriented CdTe, the morphologies are similar to that grown on Si  $\langle 111 \rangle$ . On both films, the most noticeable feature is the large number of micron size speckles. Aside from this structure, the rest of the film is very smooth for that deposited on CdTe  $\langle 111 \rangle$ A and very rough for that deposited on Si  $\langle 111 \rangle$ . Parallel twin lines are also visible on the film grown on CdTe  $\langle 111 \rangle$ A.

The density of these speckles varies from run to run, ranging from  $10^7/\text{cm}^2$  to  $10^4/\text{cm}^2$ . The exact origin is not yet known. Further analysis will be carried out to understand their cause in order to improve the surface morphology.

2.2.2.2.2. X-Ray Diffraction Analysis. X-ray Laue backscattering analysis is not suitable for these thin film because of the interference with the diffraction from the CdTe substrate. We used x-ray diffraction study to gain some structural information.

X-ray diffraction spectra were taken from 20° to 42° (2 $\theta$ ) by using the  $\text{CuK}_\alpha$  x-ray source. This range is chosen because of the presence of the following diffraction peaks of interest:



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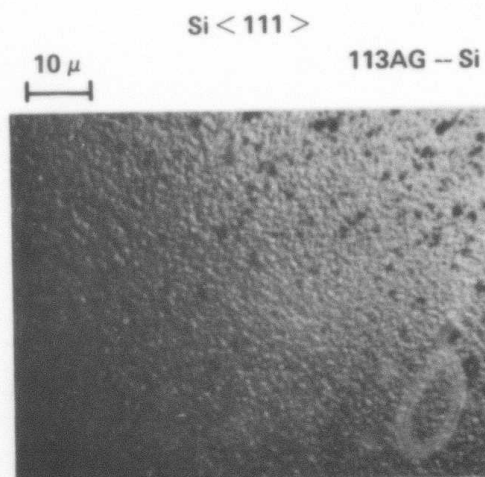
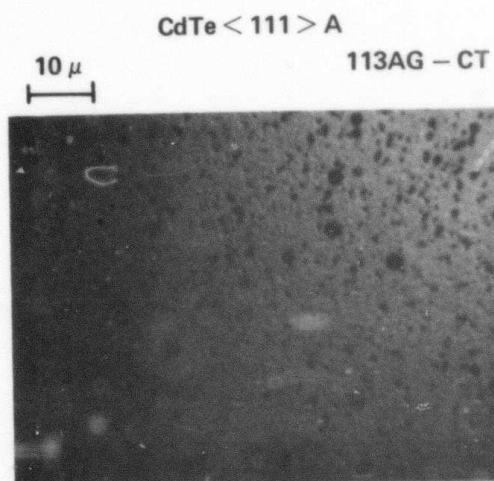


Fig. 10 Surface morphology of HgCdTe deposited on CdTe  $\langle 111 \rangle$  A and Si  $\langle 111 \rangle$ .



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Identification	Location ( $2\theta$ )
HgCdTe $\langle 111 \rangle$	$23.8^\circ$
HgCdTe $\langle 220 \rangle$	$39.4^\circ$
Si $\langle 111 \rangle$	$28.4^\circ$
Te <sub>2</sub> $\langle 101 \rangle$	$27.6^\circ$
Te $\langle 102 \rangle$	$38.3^\circ$

Powder spectra of  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  and tellurium were used as standards. The relative intensities of the two  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  peaks is an indication of the degree of orientation and crystallinity. The presence or the absence of the tellurium peaks can reveal whether the film has only a single phase (HgCdTe) or two phases (HgCdTe and tellurium). The silicon  $\langle 111 \rangle$  peak serves as an internal calibration. By comparing the Si  $\langle 111 \rangle$  peak with the  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$   $\langle 111 \rangle$  peak for films deposited on a Si  $\langle 111 \rangle$  substrate; we were able to estimate, for the case of  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  deposited on CdTe, the amount of the substrate contribution to the  $\langle 111 \rangle$  diffraction peak. It turned out that for a 5  $\mu\text{m}$  thick film on a CdTe  $\langle 111 \rangle$  peak, the CdTe  $\langle 111 \rangle$  substrate contribution to the  $\langle 111 \rangle$  peak at  $2\theta = 23.8^\circ$  was less than 0.2% and hence negligible.

2.2.2.2.1 Calibration Experiment. The method which was used to determine the CdTe substrate contribution to the diffraction intensity at  $2\theta = 23.8^\circ$  is worthy to mention. The procedure will be described in the following.



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A 5  $\mu\text{m}$  thick HgCdTe film was deposited on a piece of  $\langle 111 \rangle$  oriented Si. The sample was cut into two halves. On one piece, 45% of the film was etched to expose the bare Si surface. The other piece was completely covered with  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ . X-ray diffraction of both the Si  $\langle 111 \rangle$  peak and the HgCdTe  $\langle 111 \rangle$  peak were taken. The relative intensities are

Sample	HCT $\langle 111 \rangle$	Si $\langle 111 \rangle$
1. 100% HCT/Si	75	5.8
2. 55% HCT/Si 45% Si	46	1360

Let us designate:

$I_2$ : Diffraction intensity per unit area of the Si  $\langle 111 \rangle$  peak from bare silicon surface

$\alpha I_S$ : Diffraction intensity per unit area of the Si  $\langle 111 \rangle$  peak from silicon covered with 5  $\mu\text{m}$  thick  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  film

$I_H$ : Diffraction intensity per unit area of the HCT  $\langle 111 \rangle$  peak

$A_1$ : Total area of sample 1

$A_2$ : Total area of sample 2.



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Following relationships can be established.

For sample 1

$$A_1, \alpha I_S = 5.8$$

$$A_1, I_H = 75$$

For sample 2

$$0.45 A_2 I_S + 0.55 A_2 \alpha I_S = 1360$$

$$0.55 A_2 I_H = 46.$$

By arranging the equations and cancelling  $A_1$ ,  $A_2$  and the ratio  $I_H/I_S$ . We can obtain  $\alpha$ :

$$\alpha = 0.002 \text{ or } 0.2\%.$$

Physically,  $\alpha$  represents the fraction of total x-ray which penetrates through a 5  $\mu\text{m}$  thick HCT film onto the Si substrate at  $2\theta = 28.4^\circ$ , then reflects at the same angle through the HCT film to be detected. The effective thickness which the x-ray has to penetrate through is  $2d \cos \theta \approx 25 \mu\text{m}$ . For CdTe substrate, the Bragg angle is smaller at  $2\theta = 23.8^\circ$  corresponding to an effective HCT thickness of 28  $\mu\text{m}$  and therefore smaller  $\alpha$  value (i.e., less than 0.2%). Therefore we conclude that the CdTe substrate interference in the  $\langle 111 \rangle$  peak is negligible.



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#### 2.2.2.2.2. X-Ray Diffraction Results

A. Stoichiometric Films. Figures 11 thru 13 show the diffraction spectra of three  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  films, 5  $\mu\text{m}$  thick, deposited on various substrates at different temperatures.

In first case, the film was deposited on a Si  $\langle 111 \rangle$  substrate at 25°C. The most predominant peak is from the HCT  $\langle 111 \rangle$  orientation. Other orientation such as  $\langle 220 \rangle$  was also present but with weaker intensity. The ratio of the two peaks is 10:1. Within the detection sensitivity no separate tellurium phase was observed.

Films deposited on a Si  $\langle 111 \rangle$  substrate at 125°C showed a more preferential  $\langle 111 \rangle$  orientation. The ratio of  $\langle 111 \rangle$  to  $\langle 220 \rangle$  is 700:1. The width of the  $\langle 111 \rangle$  peak (FWHM) is 6 minutes. Again, no separate phase of tellurium can be observed.

The film deposited on a CdTe  $\langle 111 \rangle$ A substrate at 125°C showed only one diffraction peak at  $\langle 111 \rangle$ . The width is 3.6 minutes which is the resolution limit of the x-ray diffractometer.

Films on sapphire substrates also exhibit a preferred  $\langle 111 \rangle$  texture similar to those deposited on silicon.

In summary, LADA HgCdTe films always show a  $\langle 111 \rangle$  texture. The preferential orientation in this direction is enhanced by higher substrate temperature and the use of the lattice match substrate such as CdTe  $\langle 111 \rangle$ A. For film deposited on CdTe  $\langle 111 \rangle$ A at 125°C, the diffraction spectrum show a



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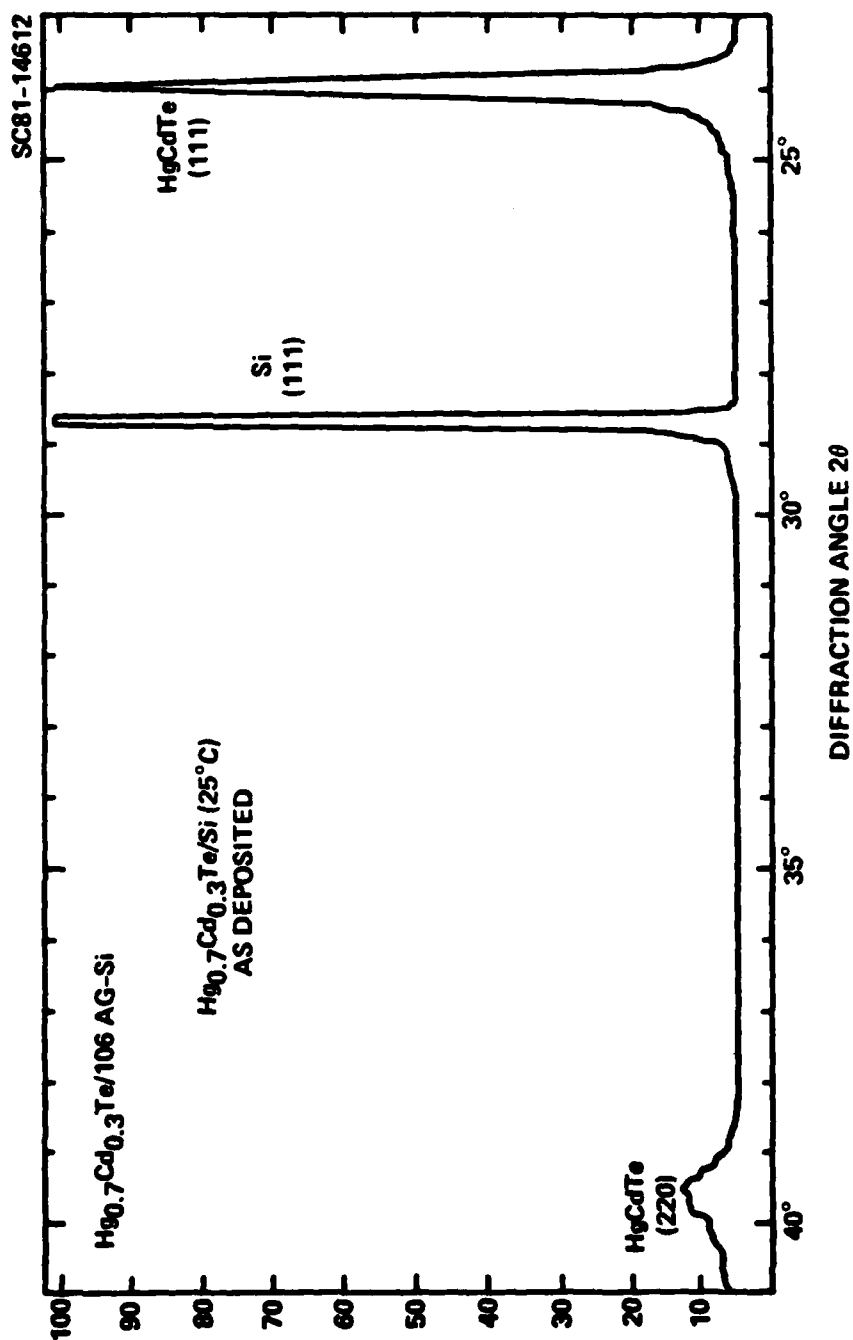


Fig. 11 X-ray diffraction of a HgCdTe film deposited on Si  $\langle 111 \rangle$  substrate at 25°C.



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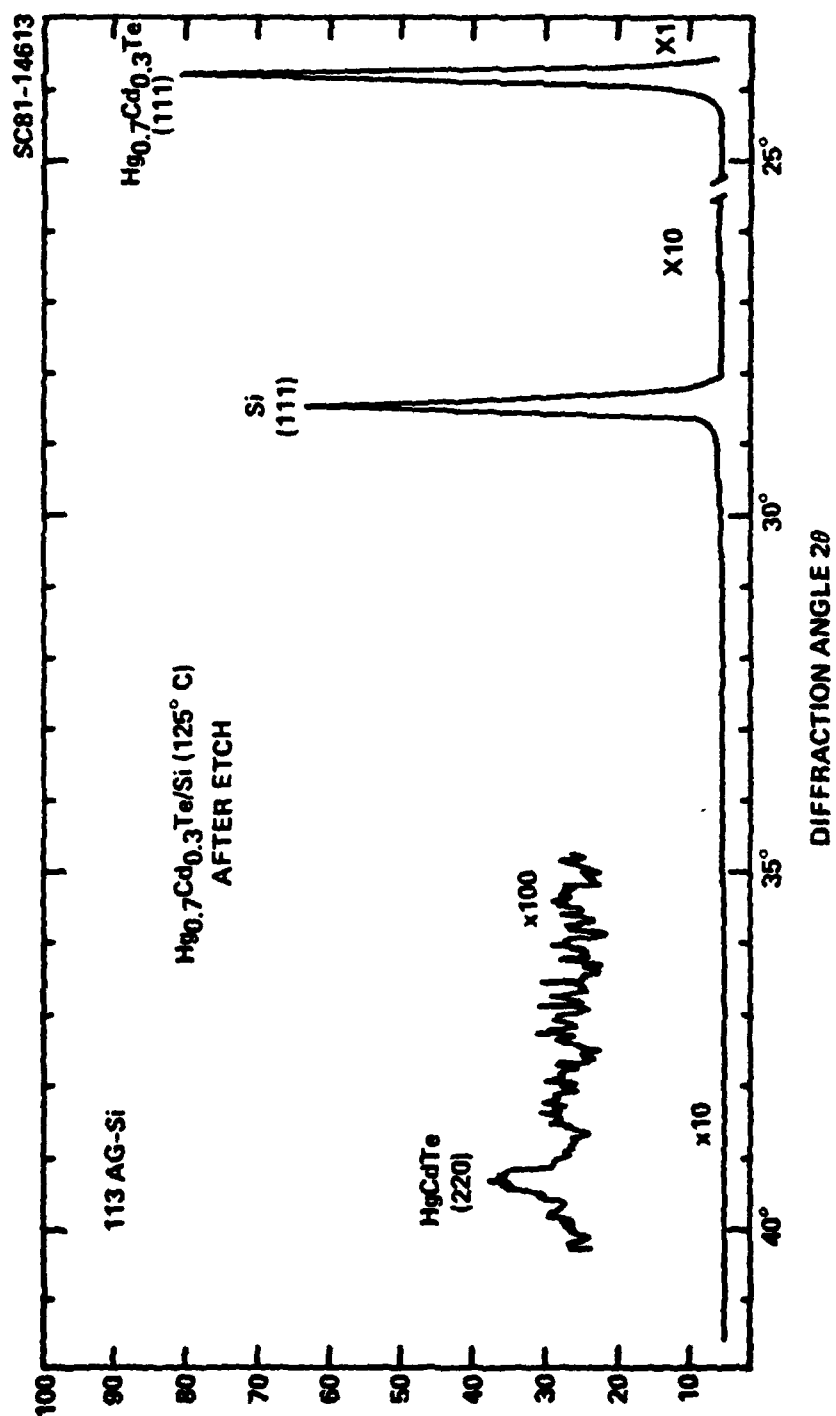


Fig. 12 X-ray diffraction of a HgCdTe film deposited on Si  $\langle 111 \rangle$  substrate at 125°C.



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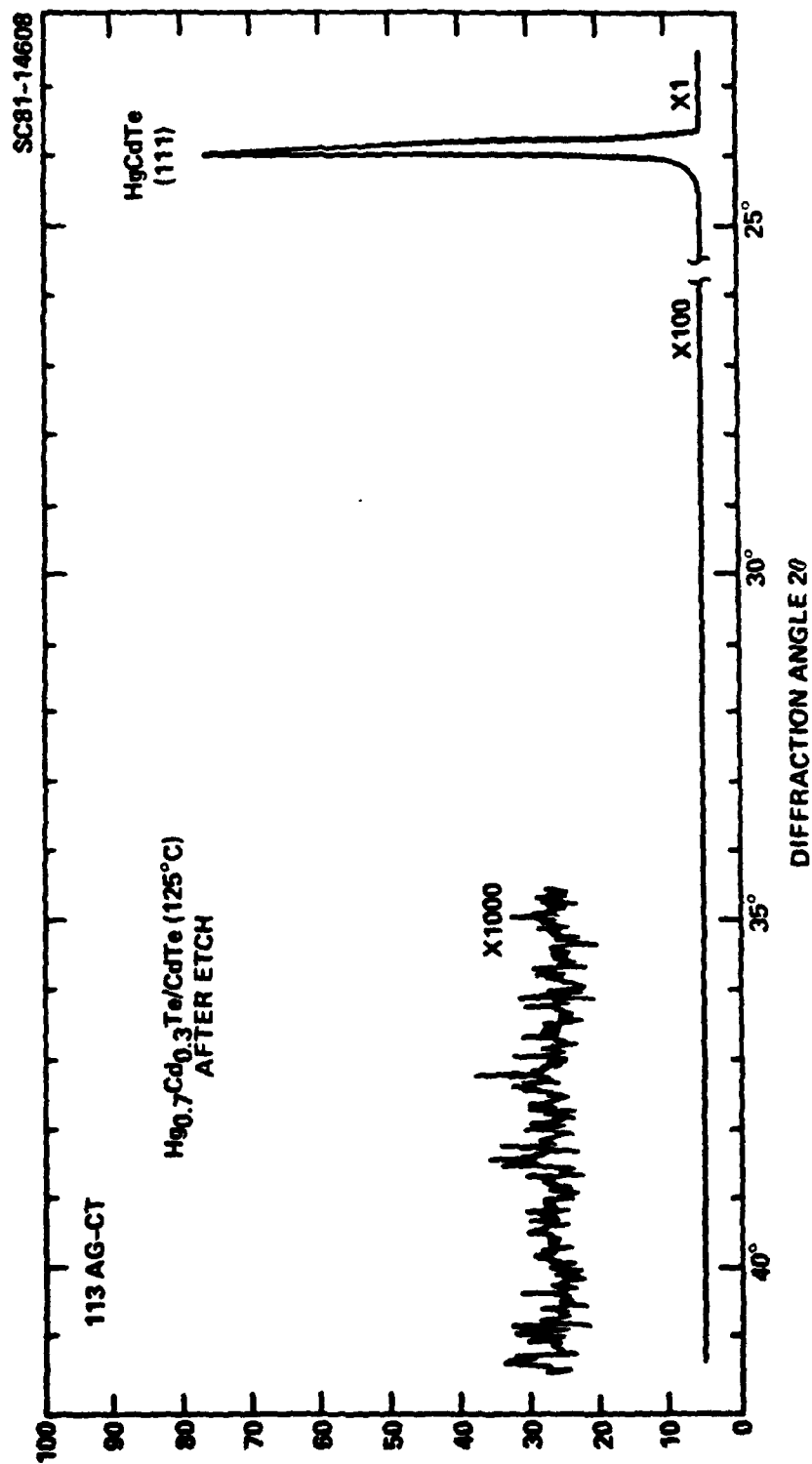


Fig. 13 X-ray diffraction of a HgCdTe film deposited on CdTe <111>A substrate at 125°C.



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single peak with narrow FWHM, suggesting the structural property of this film approaching that of a single crystal.

B. Non-Stoichiometric Films. As discussed in Section 2.2.1.1, films deposited in an environment with insufficient Hg backpressure are non-stoichiometric (i.e.,  $(\text{Hg}_{1-x}\text{Cd}_x\text{Te})_y\text{Te}_{1-y}$ ,  $y < 1$ ), accompanied by the formation of a second phase of free tellurium. X-ray diffraction analysis of such films did reveal this second phase. It also showed some evidence about the competition for lattice site between the two phases during film formation. The details will be discussed in the following.

Figure 14 shows an x-ray diffraction spectrum of a film deposited on a CdTe <111>A substrate at 125°C. The Hg backpressure during the deposition process was only  $4 \times 10^{-5}$  torr, not high enough to fully compensate the Hg deficiency. Consequently, the resultant film composition is  $\text{Hg}_{0.6}\text{Cd}_{0.3}\text{Te}$  (or  $(\text{Hg}_{0.6}\text{Cd}_{0.3}\text{Te}_{0.9})\text{Te}_{0.1}$ ) with 10% free tellurium. X-ray diffraction pattern shows the presence of two phases: a free tellurium phase with peaks ( $2\theta$ ) at  $27.7^\circ$  (<101>) and  $38.4^\circ$  (<102>) and a HCT phase with peaks at  $23.8^\circ$  (<111>) and  $39.5^\circ$  (<220>). The tellurium phase, although only amounts to 10% of the total tellurium, severely perturbs the formation of the HCT. The HgCdTe peaks are very broad (FWHM = 40 min) and do not show any preferred orientation. The intensity ratio of the <111> and <220> peaks is similar to the value for a random powder sample.

The increase of the free tellurium phase can degrade the crystallinity of the HCT phase. In one extreme case, we deposited a film onto a Si

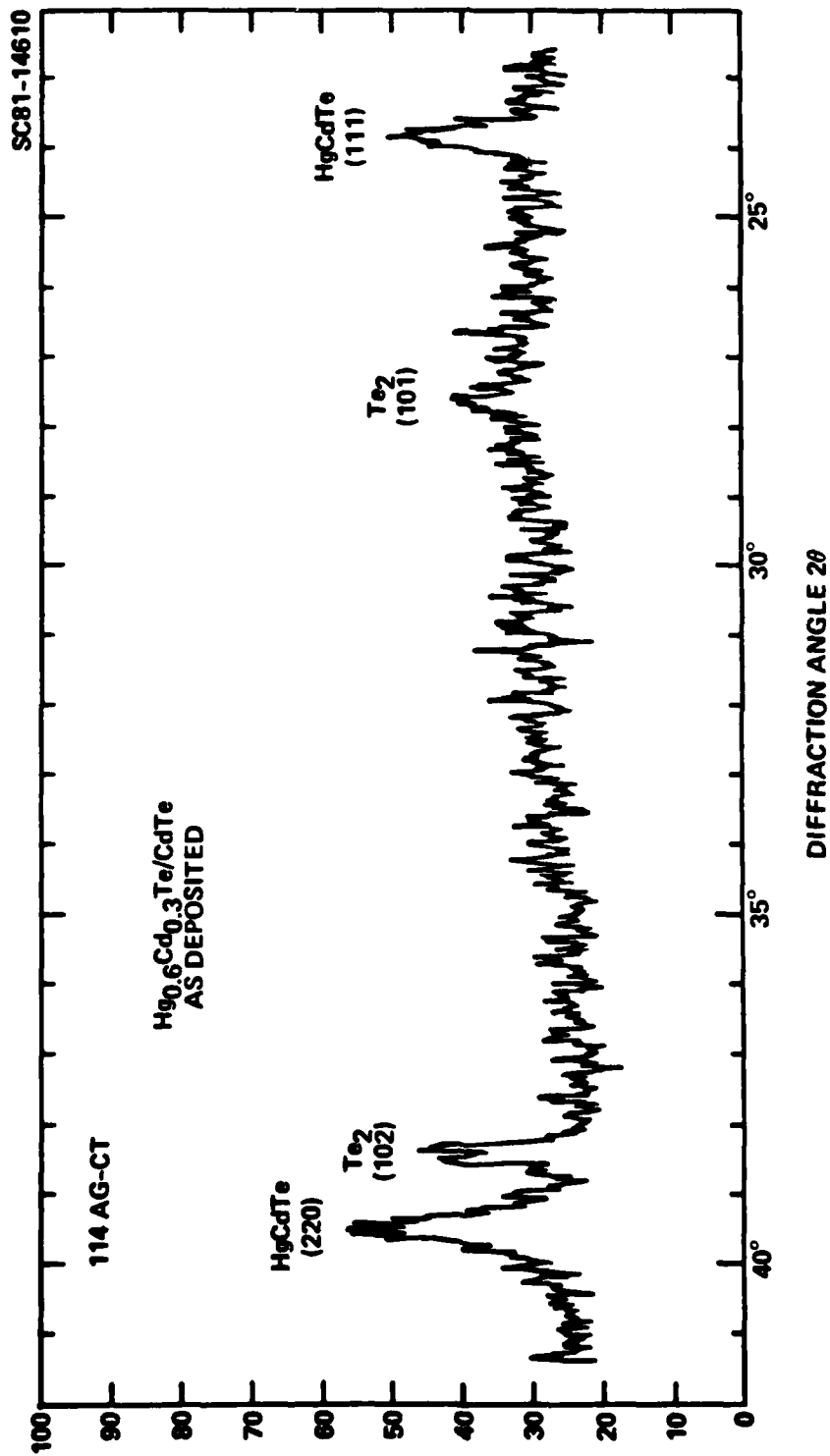


Fig. 14 X-ray diffraction of a non-stoichiometric HgCdTe film with about 10% free tellurium.



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$\langle 111 \rangle$  substrate at 125°C in a Hg free vacuum environment. Its composition was determined by EDAX to be  $\text{Hg}_{0.06}\text{Cd}_{0.3}\text{Te}$  (i.e.,  $(\text{Hg}_{0.06}\text{Cd}_{0.3}\text{Te}_{0.36})\text{Te}_{0.64}$ ). More than half of the tellurium is in the free elemental form. X-ray diffraction spectrum is shown in Fig. 15. It does not show any peaks of either phase. The film is amorphous.

#### 2.2.2.3 Electrical Properties

Films with  $x = 0.3$  composition were characterized electrically by Hall measurements at 300K and 77K. All films were n-type which was expected for a growth at such low substrate temperature. Some films were also annealed in a closed ampoule containing Hg at 210°C in order to improve the electrical properties. Films ( $x = 0.3$ ) on CdTe substrates at 300K had carrier concentration and mobility from  $3 \times 10^{16}/\text{cm}^3$  and 700-1200  $\text{cm}^2/\text{Vsec}$ , respectively. At 77K, these parameters were too low to be measured. After annealing in a closed ampoule containing Hg, the carrier concentration at 77K was at  $1-2 \times 10^{17}/\text{cm}^3$  and the mobility ranged from 3500-6500  $\text{cm}^2/\text{Vsec}$ . Films grown on Si substrates showed similar carrier concentrations, but the mobilities were about four times lower. From these results we can conclude:

1. The electrical properties of the LADA films are similar to the  $\text{MBE}^2$  films. Although the growth conditions and experimental approaches are very different.
2. The carrier mobilities are much lower than the bulk material.



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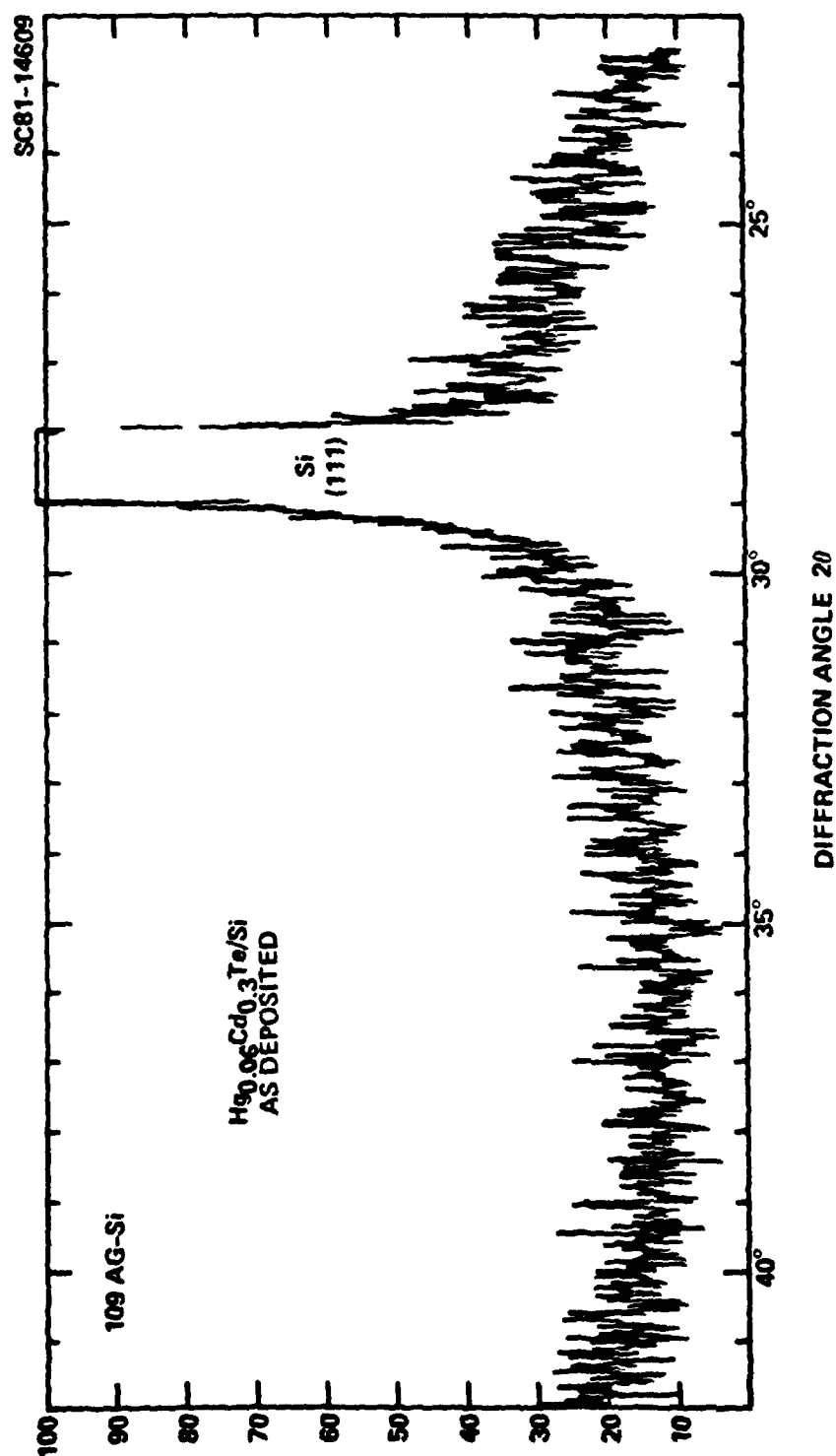


Fig. 15 X-ray diffraction of a non-stoichiometric HgCdTe film containing 64% free tellurium.



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3. Films deposited from  $(\text{HgTe})_{0.7}/(\text{CdTe})_{0.3}$  mixture and from  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  bulk crystal have the similar electrical properties.

Some films were also annealed at high temperature near  $400^{\circ}\text{C}$  in attempt to convert them to p-type. However, little success was made as most films remained n-type. Only in one occasion, for a  $x = 0.3$  film deposited from  $(\text{HgTe})_{0.7}/(\text{CdTe})_{0.3}$  powder mixture target, we were able to convert it to p-type upon annealing. The hole concentration and mobility of this film at 77K were  $1 \times 10^{17}/\text{cm}^3$  and  $90 \text{ cm}^2/\text{V-sec}$ , respectively.



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### 3.0 FUTURE PLANS

Future plans can be divided into three areas: to improve the film surface morphology, to improve the electrical properties and to improve the quality of the films grown on foreign substrates.

#### 3.1 Film Surface Morphology

At this development stage, the surface morphology is not reproducible. Some films exhibit specular surface, yet others are very rough with the presence of speckles as shown in Fig. 10. The cause is still unknown. Our first task is to identify the composition of these speckles and then to deduce the origin of their formation. Subsequent efforts will include the optimization of the growth condition, substrate preparation procedure and perhaps most important of all, the optimization of laser parameters.

#### 3.2 Electrical Properties

From the Hall measurement results, following intricate questions rise:

1. Why are the as-grown film all n-type? Is the n-type conduction a result of Hg interstitial or Te vacancy?
2. Why do the films not convert to p-type after post-growth annealing? Is it an impurity related problem?



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3. Why is the mobility relatively low compared to bulk and LPE materials? Is it related to the structural imperfection due to the low growth temperature?

In order to understand some of these questions and to improve the film quality, following actions will be taken:

1. To improve substrate preparation procedure by trying the following:
  - a. Better surface etching procedure
  - b. Heat treating the substrate at high temperature prior to deposition
  - c. In situ laser cleaning
  - d. Depositing a CdTe buffer layer.
2. To obtain high growth temperature by increasing the Hg backpressure to  $10^{-3}$  torr.
3. To understand the factors which limits the electrical properties by carrying out in-depth characterization (e.g., SIMS, SAM, TEM, SEM, etc.) and comparing the results with LPE layers.
4. To optimize the laser condition.



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5. To optimize the post annealing conditions by varying temperature, time and the amount of background Hg and Te partial pressure.

### 3.3 Film Grown on Foreign Substrates

This emphasis on this effort will be less than the previous one. InSb will be used as a substrate material. It is lattice match with the HgCdTe system and at the low growth temperature used LADA, indium diffusion into HgCdTe should be negligible.



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#### 4.0 REFERENCES

1. A.W. Stephens, T.J. Zrebiec and V.S. Born, Mat. Res. Bull. 9, 1427 (1974).
2. J.P. Faurie and A. Millon, J. Cryst. Growth, 54, 585 (1981).
3. For example: R. Cornely, L. Suchow, T. Gabara and P. Diodato, IEEE Trans. Elect. Dev. ED27, 29 (1980).